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REACTION OF 2,2-DIMETHYLTETRAHYDRODICYCLOPENTADIENE WITH ALUMINUM CHLORIDE: THE ADAMANTANE REARRANGEMENT

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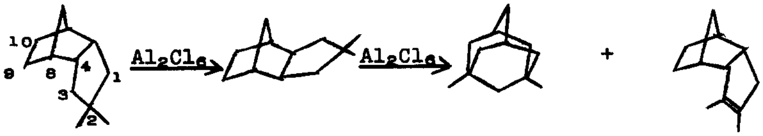
Both endo-(I) and exo-(II) tetrahydrodicyclopentadienes are isomerized to adamantane (III) by strong Lewis acids such as aluminum chloride, aluminum bromide and boron trifluoride (1,2). This reaction appears to be general for tricyclic, saturated alkanes containing ten or more carbon atoms (2,3). For example, several methyl and dimethyl tetrahydrodicyclopentadienes give 1-methyl- and 1,3-dimethyladamantanes, respectively (4). In the presence of hydrogen halides I yields additionally trans-decalin(IV)(5,6) and 9-exo-halo tetrahydro-exo-dicyclopentadiene (V) (5).

I II III

IV

V



VI VII VIII IX

The *endo*-(VI) and *exo*-(VII) 2,2-dimethyltetrahydrodicyclopentadienes were prepared by the catalytic hydrogenation of the corresponding 2,2-dimethyl-1,2-dihydrodicyclopentadienes (7). Alkane VI (0.5 g.) in cyclohexane (5 ml.) was refluxed with aluminum chloride (0.25 g.) for eight hours. The mixture was treated with water and analyzed by gas-liquid partition chromatography between helium and polypropylene glycol. The products were identified by comparison with authentic samples*. With a 4 ft. x 4 mm. column, the retention times (minutes) at 100° were VIII, 4.9; VII, 5.8; VI, 7.0; IX, 11.2. The product contained 66% VII, 12% 1,2-dimethyl-9,10-dihydro-*endo*-dicyclopentadiene (IX), 6% 1,3-dimethyladamantane (VIII) and two unidentified products 10% and 7%.

The alkene IX was the major product of the reaction of both the *endo*- and *exo*-2,2-dimethyl-1,2-dihydrodicyclopentadienes with phosphoric acid (5,8). Structure IX was confirmed by oxidation to the corresponding diketone which was independently synthesized (5,8). The *endo* to *exo* rearrangement of VI to VII is analogous to that of I to II under similar conditions (1), but, unlike I, VII rearranged further. This is consistent with the generalization that rearrangement to the adamantane structure is often faster for homologs of adamantane than for adamantane itself (2).

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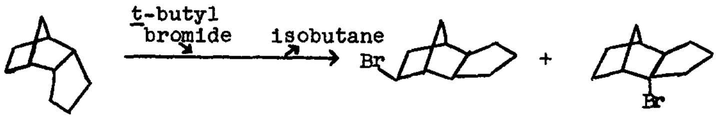
* A sample of 1,3-dimethyladamantane for comparison purposes was kindly supplied by Professor P. von R. Schleyer.

In the absence of solvent more rearrangement was observed. Alkane VI (0.5 g.) stirred with aluminum chloride (0.13 g.) at room temperature was isomerized firstly to VII, and then to a mixture of VIII and IX. Samples were withdrawn, and the progress of the reaction was followed by gas-liquid partition chromatography as described above. The conversion of VI to VII was complete in one hour. Subsequently the concentration of VIII gradually rose to 73% (after 50 hours) as the concentration of VII dropped to 0%. The concentration of IX reached a plateau value of about 30% when VIII was 36%. Possibly IX is removed by polymerization, and thus reaches a steady state concentration. Alternatively, IX is formed only when the catalyst is fresh. Three unidentified minor products (<5%) were observed.

Since no intermediates in the conversion of VII to VIII appeared in large quantities it seems likely that the first step in the reaction is the slow step, which might be the 4,9-alkyl shift on VI ionized at C_9 (1). This was also the case in the formation of other substituted adamantanes (4). The appearance of alkene IX during the formation of 1,3-dimethyladamantane from other precursors was not reported (4). Alkene IX is possibly derived via a 3,9-hydride shift on VI ionized at C_9, with concomitant 2,3-methyl shift and subsequent elimination. Thus the special position of the gem-dimethyl group in VI might facilitate the formation of the extremely stable alkene IX. There is also evidence for this 3,9-hydride shift in the reactions of the 1,2-dihydrodicyclopentadienes and the 2,2-dimethyl-1,2-dihydrodicyclopentadienes with phosphoric acid, and the pyrolysis of the methyl xanthate of 9-hydroxytetrahydrodicyclopentadiene (5,8).

The observed products appear to be derived via rearrangements originating from ionization at the C_9 position. Although it does not follow that hydride is most readily abstracted from this position, the experiment described below indicates that this is indeed the case.

A mixture of alkane I (23 g.), tert-butyl bromide (26 g.) and aluminum bromide (3 g.) was stirred for two hours cooled with an ice bath. The C_{10} monobromide fraction (50% yield) was analyzed by gas-liquid partition chromatography between helium and ucon polar oil, and was found to be identical with the product of isomerization of bromide X (40 g.) with aluminum bromide (8 g.) at 100°. This product contained 52% X, 21% XI and two unidentified compounds 16% and 10%.



I X XI

That all the components were monobromides of tetrahydro-exo-dicyclopentadiene (II) was shown by elemental analysis and reduction to II with sodium in ethanol and via the Grignard reagent. Bromide XI was isolated by distillation with a spinning band column (b.p. 88-91°/4.8 mm.) and the structure was tentatively assigned on the basis of lack of proton magnetic resonance absorption between 0 τ and 6.8 τ showing that XI is a tertiary bromide. Bromide X was identified chromatographically with authentic material (9). Similar rearrangements to 4-substituted tetrahydrodicyclopentadienes have been reported (1,10,11).

Since this H-Br exchange reaction was performed below room temperature, and the isomerization of X required an elevated temperature, it seems likely that the products are a direct result of the initial ionization. Since all the products had the exo ring fused configuration, the initial ionization must have been at C_9 on I to enable the endo-exo rearrangement to occur, assuming this occurred in the normal manner via the 8,9-alkyl shift. Different conclusions were reached from the analogous reaction of I with tert-butyl chloride and aluminum chloride (1).

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